

Total Scattering

Data reduction and modelling

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LA-UR 05-1010

LA-UR 06-6075

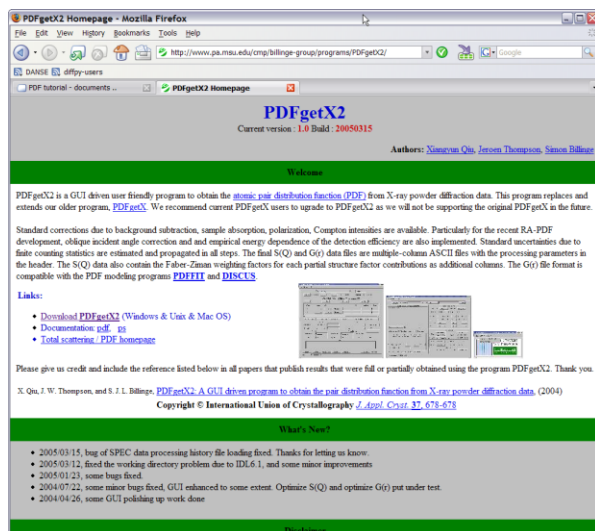
Manuel Lujan Jr.
Neutron Scattering Center
at *LANSC*



Software: Data reduction

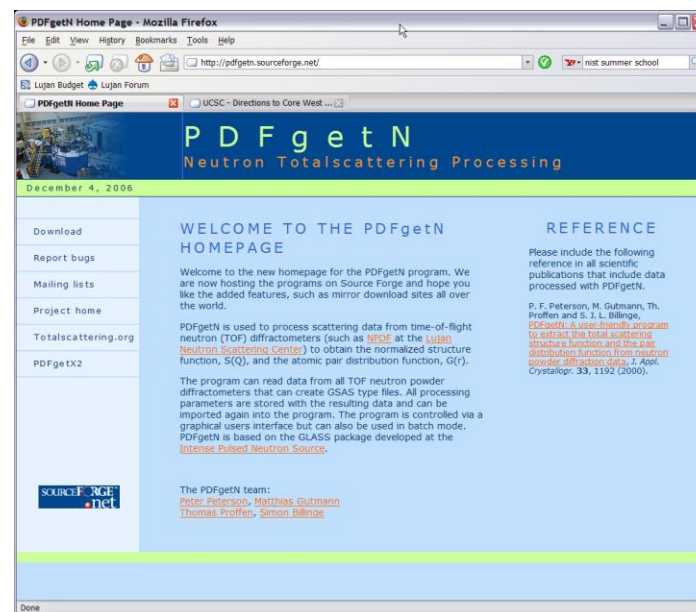
X-rays

- ❖ IDL based.
- ❖ Laboratory and synchrotron data
- ❖ <http://www.pa.msu.edu/cmp/billinge-group/programs/PDFgetX2/>



Neutrons

- ❖ GLASS package / Perl/TK frontend
- ❖ Automatic data reduction on NPDF
- ❖ <http://pdfgetn.sourceforge.net/>

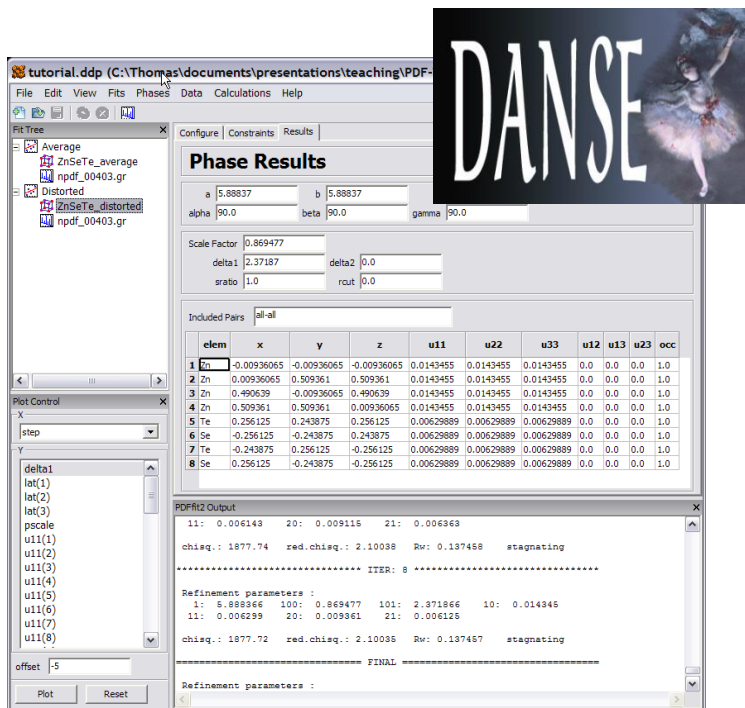


Data modeling 'PDFFIT' style

Software: Data modeling

PDFgui

- ❖ Part of DANSE project.
- ❖ <http://www.diffpy.org/>

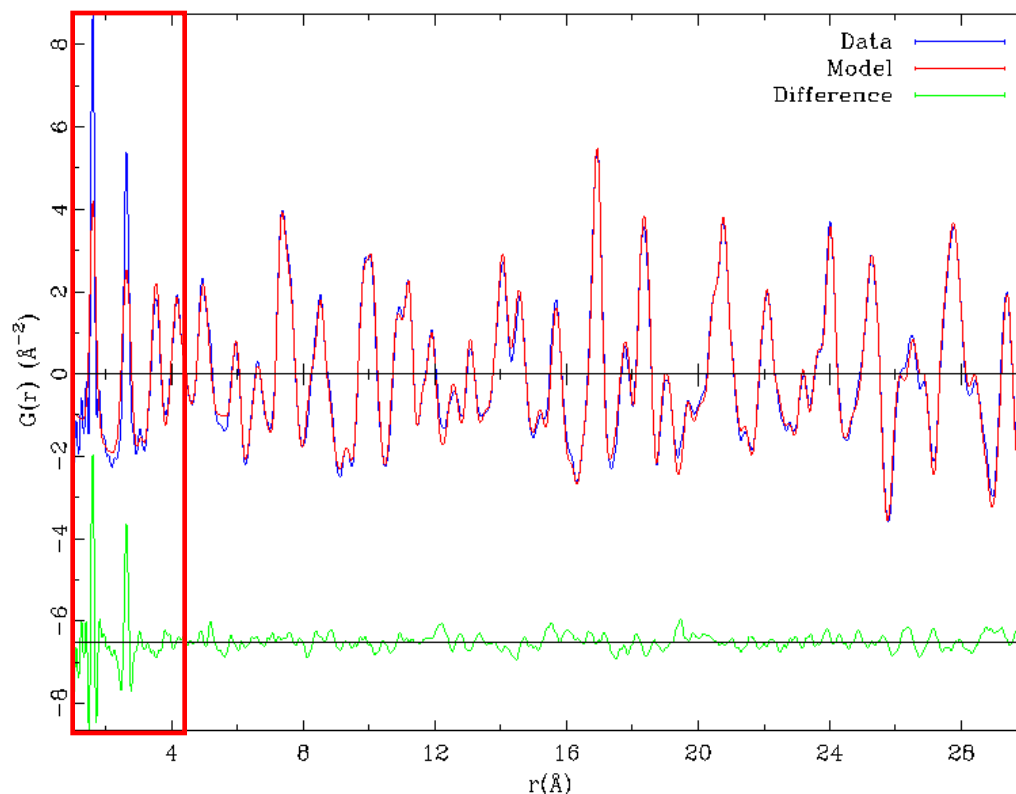


- ❖ Calculation and refinement of small model system (< 1000 atoms)
- ❖ 'Rietveld' type parameters: *lattice parameters, atomic positions, displacement parameters, ..*
- ❖ New possibilities: *Refinements as function of r range !*
- ❖ Automatic refinement of multiple datasets as function of T or x .
- ❖ Intuitive GUI.
- ❖ Engine *pdfit2* can also be used in command mode.

PDFfit: Refinement of a small structural model

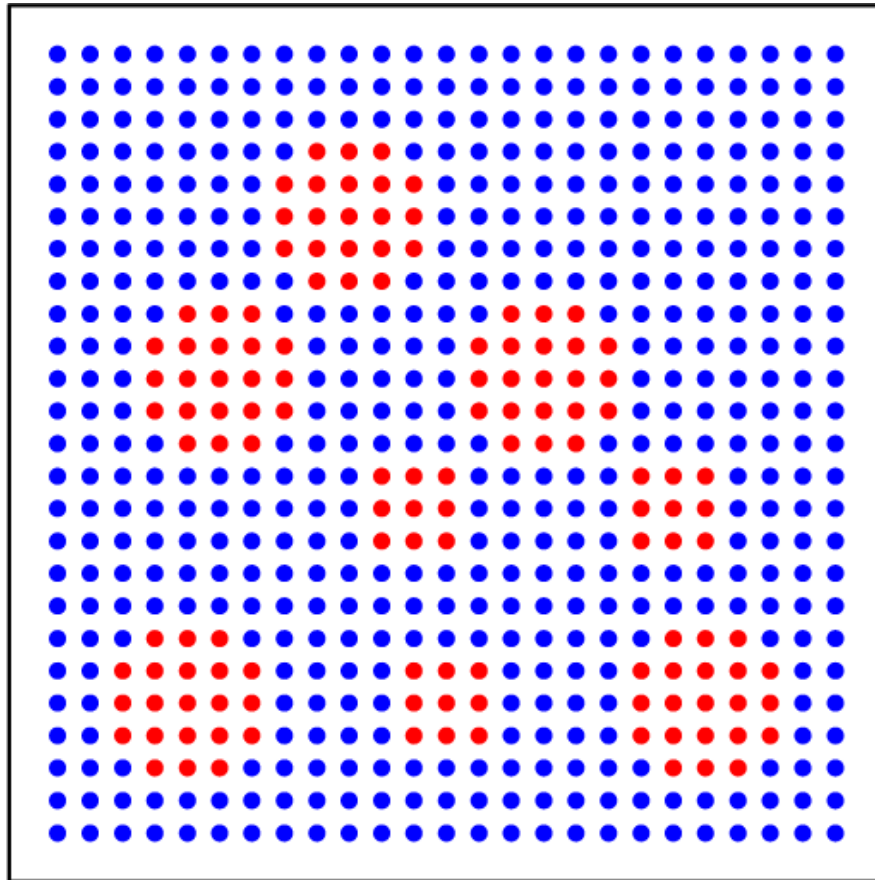
- “Real space Rietveld”
- Refinement of structural parameters: *lattice parameters, atom positions, occupancies, adp's, ..*
- Small models (<200 atoms).
- Corrections for Q_{max} , *instrument resolution, correlated motion.*
- Software: *PDFfit, PDFfit2 and PDFGui.*

Example: Is sandstone simply quartz ?



K.L. Page, Th. Proffen, S.E. McLain, T.W. Darling and J.A. TenCate, **Local Atomic Structure of Fontainebleau Sandstone: Evidence for an Amorphous Phase ?**, *Geophys. Res. Lett.* **31**, L24606 (2004).

Refinement range – length scales in structure

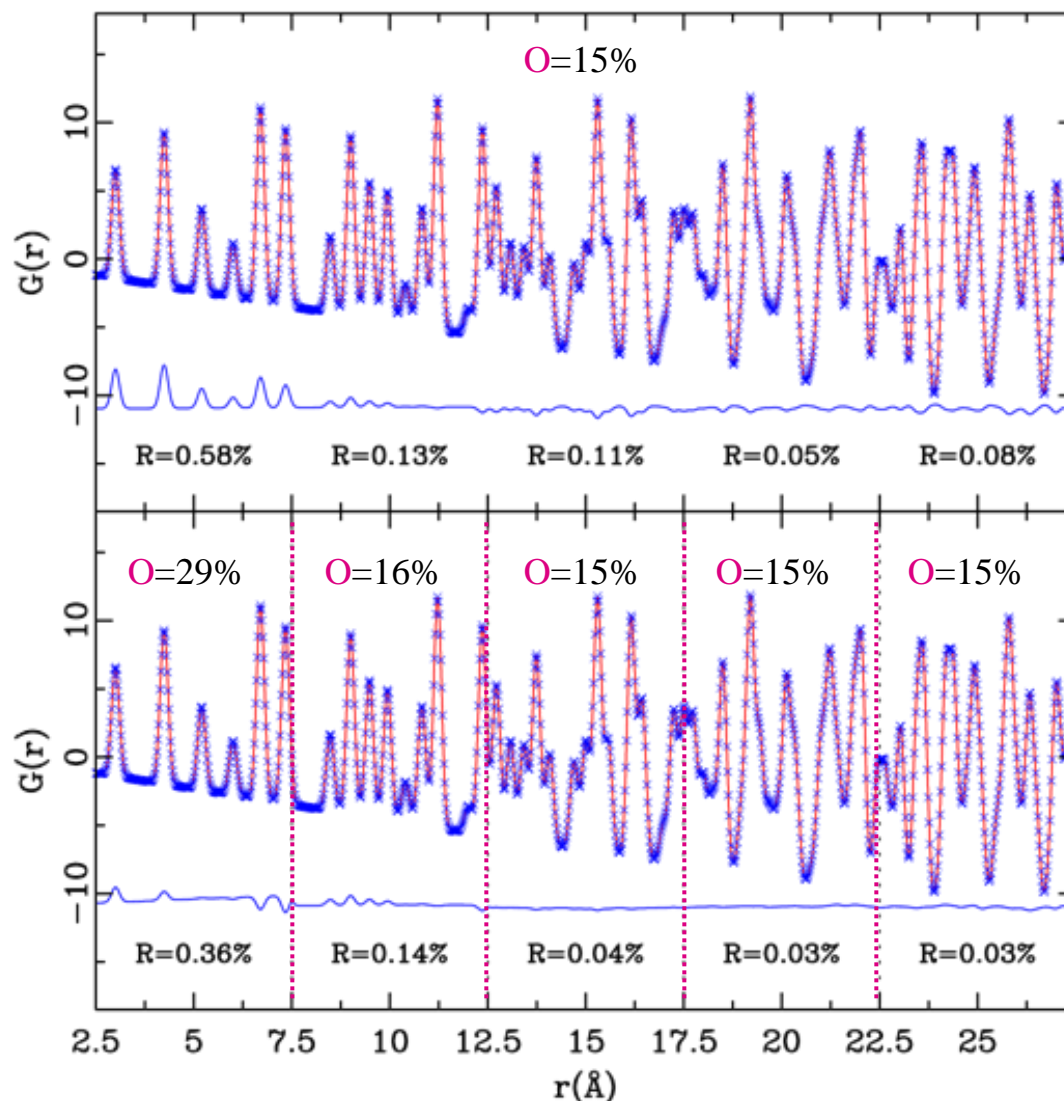


- Simulated structure of 20x20x20 unit cells.
- Matrix (M): blue atoms
- Domains (D): red atoms, spherical shape, $d=15\text{\AA}$.
- Simulated using DISCUS.

Th. Proffen and K.L. Page, **Obtaining Structural Information from the Atomic Pair Distribution Function**, *Z. Krist.* **219**, 130-135 (2004).

Refinement range – length scales in structure

- *Top:* Single-phase model with blue/red fractional occupancies (○).
- *Bottom:* Refinement of same model for 5Å wide sections.
- Extensions:
 - Multi phase models
 - Modeling of boundary
 - R-dependent refinable mixing parameters

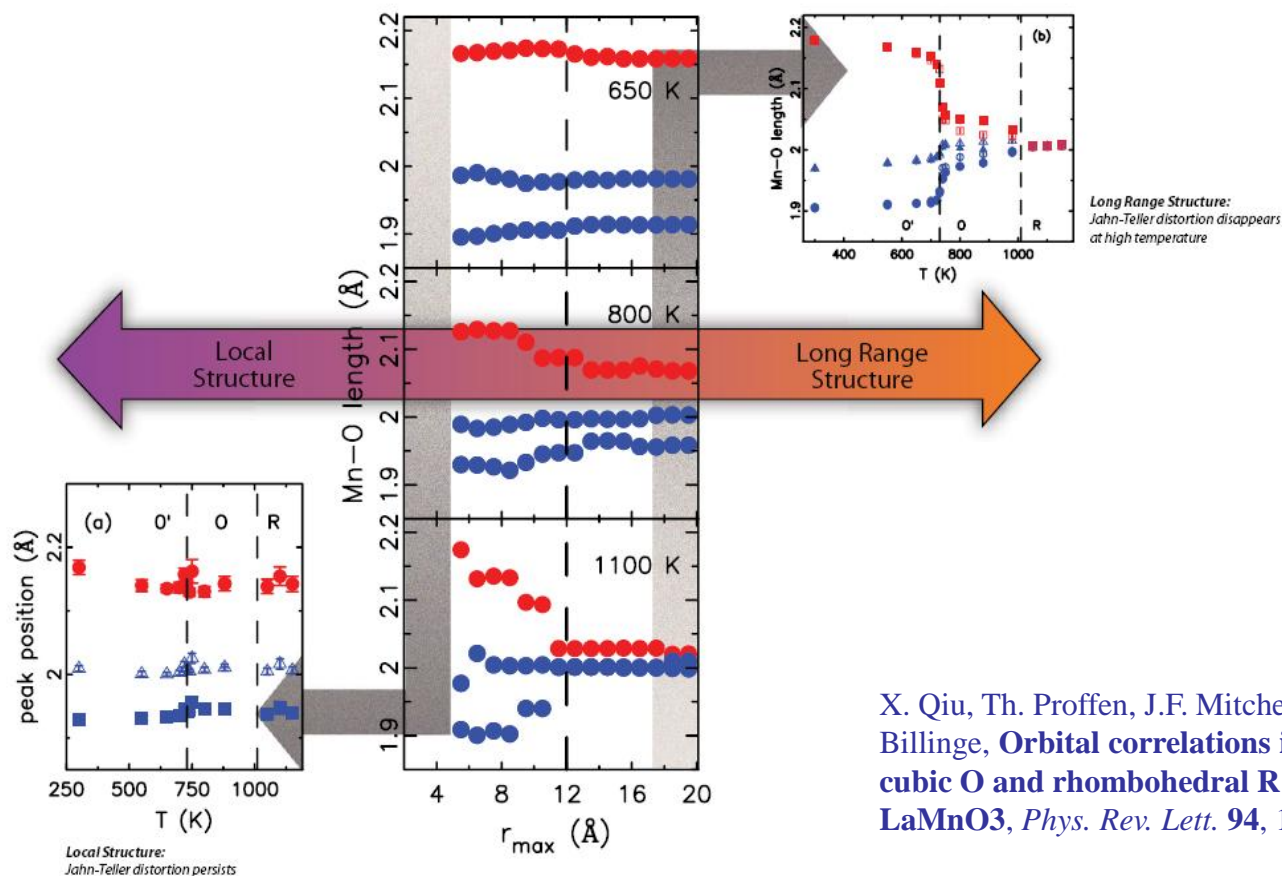


UNCLASSIFIED

Refinement range – the mystery of LaMnO_3

DISTORTED OR NOT DISTORTED?

Study of the Jahn-Teller distortion in LaMnO_3



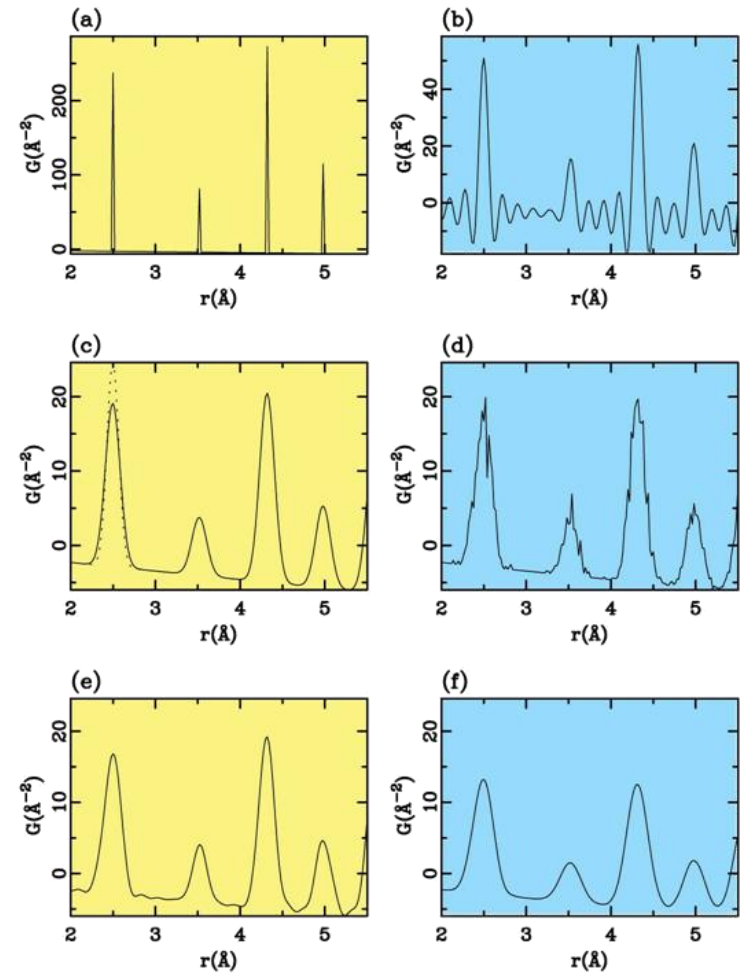
X. Qiu, Th. Proffen, J.F. Mitchell and S.J.L. Billinge, **Orbital correlations in the pseudo-cubic O and rhombohedral R phases of LaMnO_3** , *Phys. Rev. Lett.* **94**, 177203 (2005).

Calculating a PDF ..

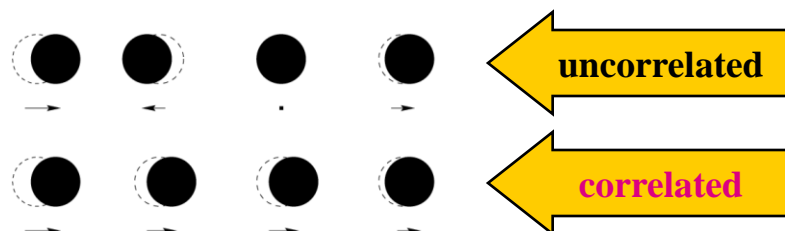
- Calculating a PDF from a structural model:

$$G(r) = \sum_{ij} \left[\frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0$$

- Thermal motion
 - Small crystal \Rightarrow convolution of $\delta(r - r_{ij})$ with distribution function (*PDFFIT*)
 - Large crystal \Rightarrow actual displacements & ensemble average (*DISCUS*)
- Termination ripples
 - Multiplication with step function in reciprocal space gives convolution with $\sin(Q_{\max} r)/r$ in real space.



PDF analysis: Analysis of individual peaks

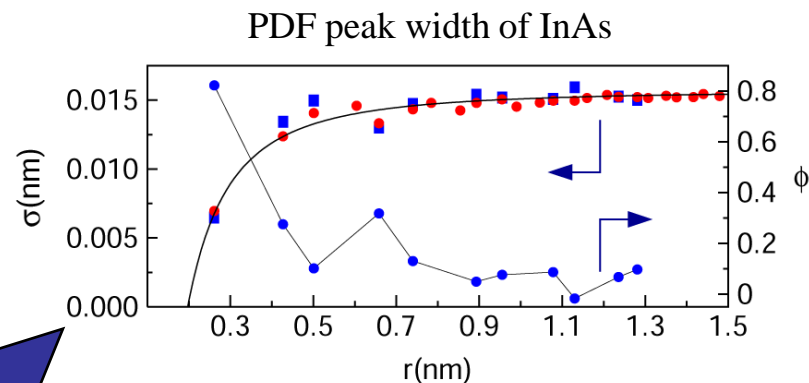


➤ Correlated motion results in sharpening of near neighbor PDF peaks.

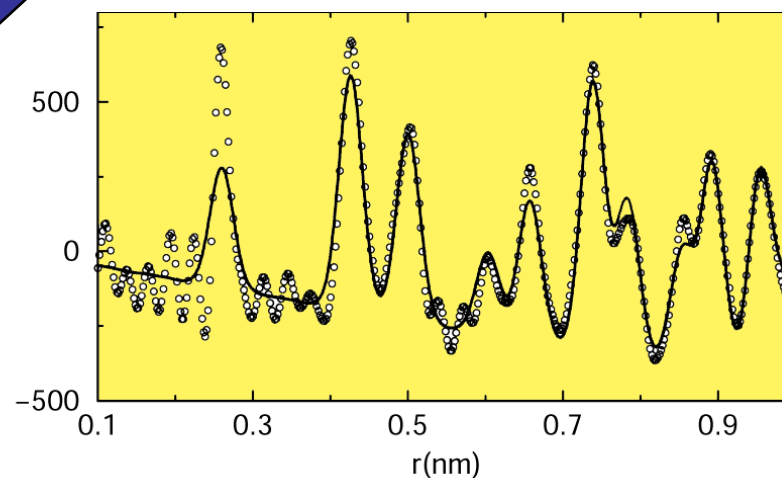
➤ Empirical correction

$$\sigma_c = \sqrt{\sigma_0 - \delta / r^2 - \gamma / r}$$

➤ *Future*: Extraction of phonons ??



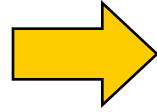
Calculated PDF without “ δ ” of InAs



Jeong et al., *J. Phys. Chem. A* **103**, 921 (1999)

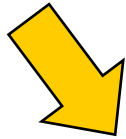
Calculating a PDF: PDFfit

PDF calculated according to



$$G(r) = \sum_{ij} \left[\frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0$$

In more detail



$$G(r_k, s) = f_s B_k(s) \sum_{p=1}^P f_p G_p(r_k, s)$$

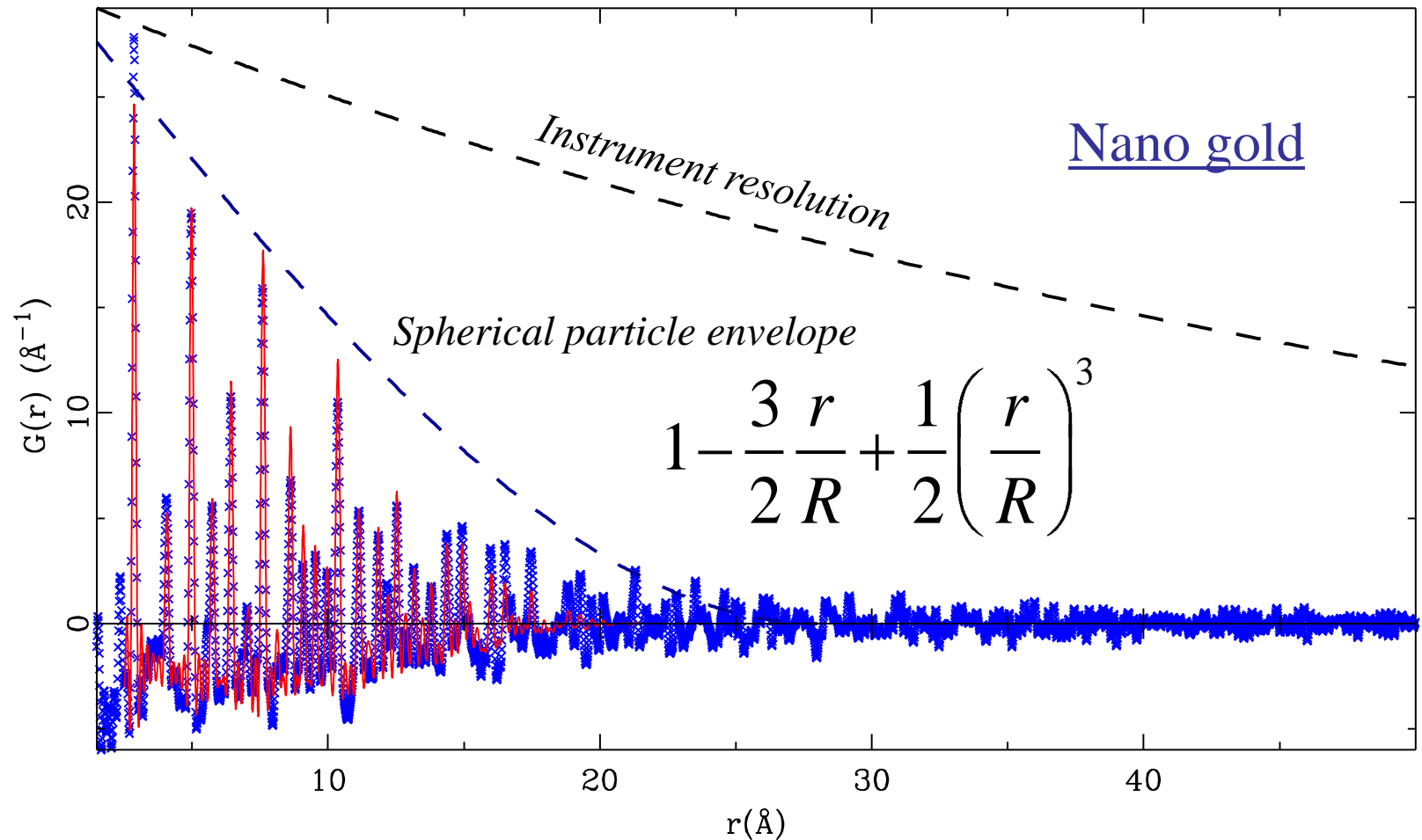
$$G_p(r_k, s) = \frac{1}{N_p r_k} \sum_i \sum_j [A_{ij}(p) \cdot T_{ij}(r_k, p)] - 4\pi r_k \rho_0(p)$$

$$B_k(s) = \exp \left[-\frac{(r_k \sigma_Q(s))^2}{2} \right]$$

$$A_{ij}(p) = \frac{c_i(p) c_j(p) b_i b_j}{\langle b \rangle^2}$$

$$T_{ij}(r_k, p) = \frac{1}{\sqrt{2\pi} \sigma_{ij}(p)} \exp \left[-\frac{(r_k - r_{ij}(p))^2}{2\sigma_{ij}^2(p)} \right]$$

Nanoparticles: Particle size

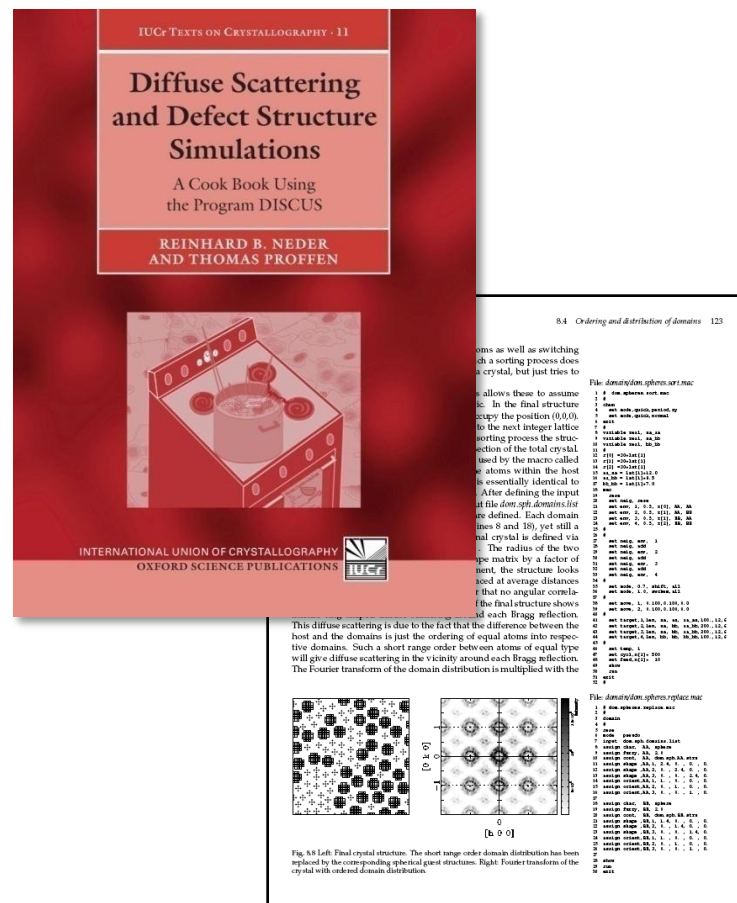
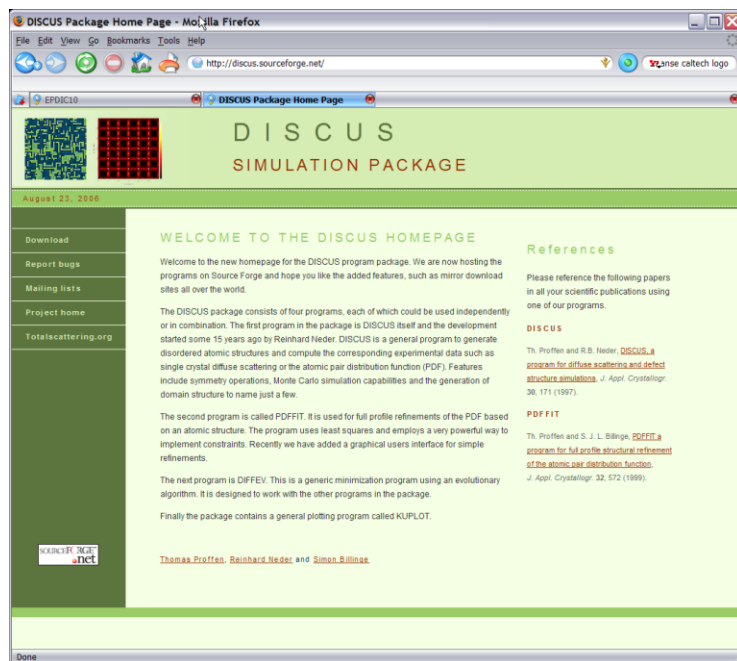


Data modeling 'DISCUS' style (RMC and DIFFEV)

Software: Data modeling

DISCUS

- ❖ Disordered materials simulations
- ❖ Refinement via DIFFEV / RMC
- ❖ <http://discus.sourceforge.net/>



Oxford University
Press, June 2008

Diffuse package: DISCUS, PDFfit and DIFFEV

- PDFfit
 - User defined relation between parameters and refinement variables.
 - Multiple structural phases and data sets (neutron and X-ray) supported.
- DISCUS
 - Calculation of Fourier transform, inverse and difference Fourier.
 - Expand structure from asymmetric unit and space group symbol.
 - Structure “statistics”: correlations, real space lots, ...
 - PDF calculations.
 - Monte Carlo simulations.
 - Reverse Monte Carlo simulations – diffuse scattering & PDF.
 - Symmetry & unit cell transformations.
- DIFFEV: General minimization using evolutionary algorithms
- KUPLOT: General plotting program
- Common features
 - Command language including loops and IF statements.
 - Online help function
 - UNIX or Windows operating system.
 - Binary or source code distribution.
 - Written in FORTRAN-77 (and some C).
- Link: <http://discus.sourceforge.net>

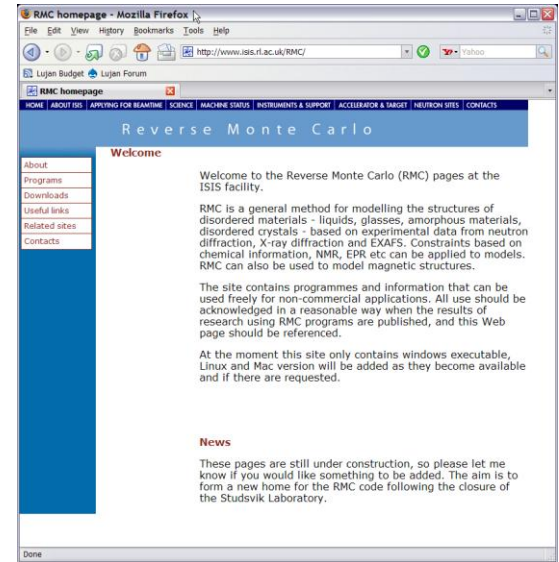
Retired !!

Th. Proffen and R.B. Neder, *J. Appl. Cryst.* **30**, 171-175 (1997).

Th. Proffen and S.J.L. Billinge, *J. Appl. Cryst.* **32**, 572-575 (1999).

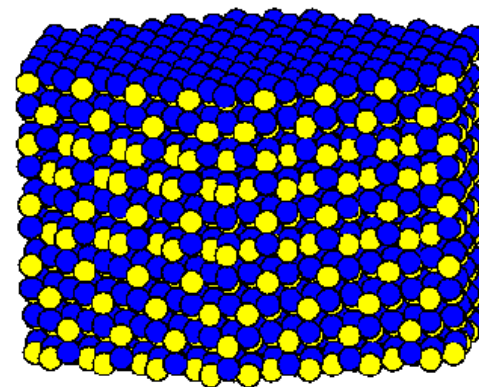
Software: RMCprofile (Matt Tucker lecture)

- RMCprofile
 - Atomic configurations ~600 to 20000+ atoms
 - Fit both X-ray and neutron $F(Q)$
 - Fit $G(r)$
 - Fit Bragg profile (GSAS tof 1,2 & 3)
 - Polyhedral restraints
 - Coordination constraints
 - Closest approach constraints
- Produce a static 3-D model of the structure (a snap-shot in time)
- Link: <http://www.isis.rl.ac.uk/RMC>

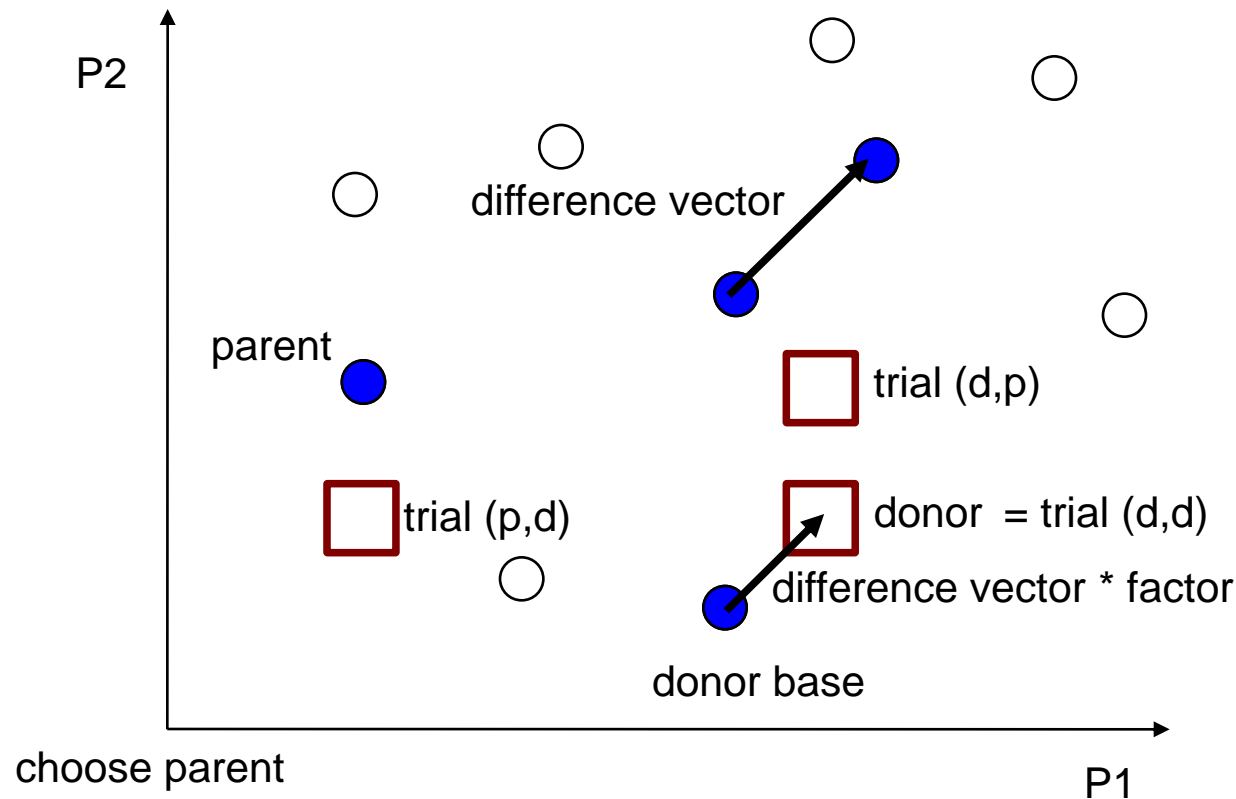


DIFFEV: Refining model parameters

- PDFfit and RMC
 - Refine structure directly in terms of atom coordinates etc ..
 - Difficult for complex systems
- Alternative
 - Refine parameters of a structural model and not each atom.
 - Example nanoparticle: *diameter, atom spacing, stacking fault probability, ...*
 - Choose minimization – here DIFFEV

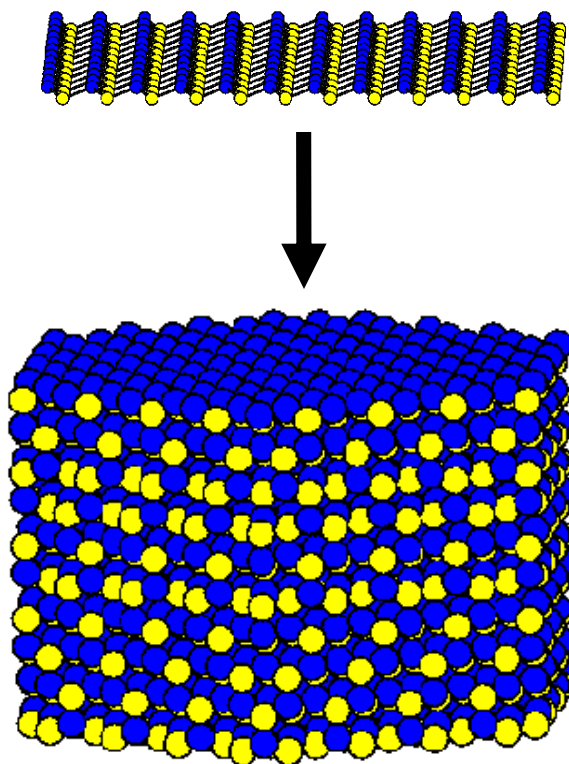


Differential Evolution



choose parent
 choose difference vector
 add to donor base to get donor
 cross-over between parent and donor
 compute cost function, keep better of parent/trial

Example: ZnSe nanoparticles - Model



$\{110\}$ and $\{001\}$

create a large single Wurtzite layer A/B

Stack along c (with faults)

Cut to proper size

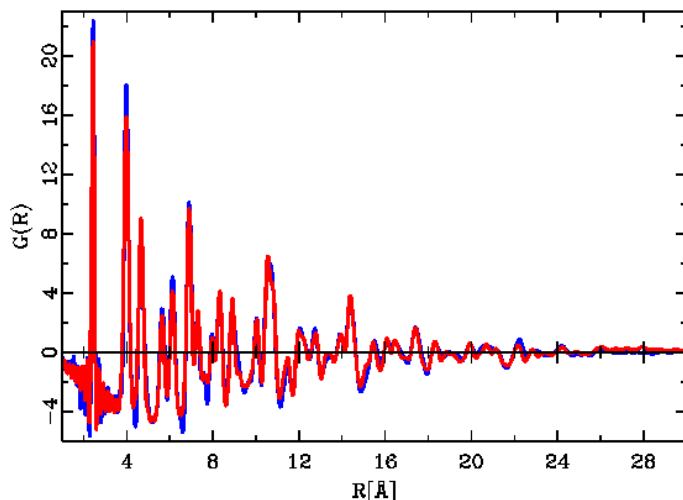
Calculate PDF / powder pattern

Repeat and average

Repeat with new set of parameter
using a Differential Evolutionary Scheme

Software: DISCUS and DIFFEV

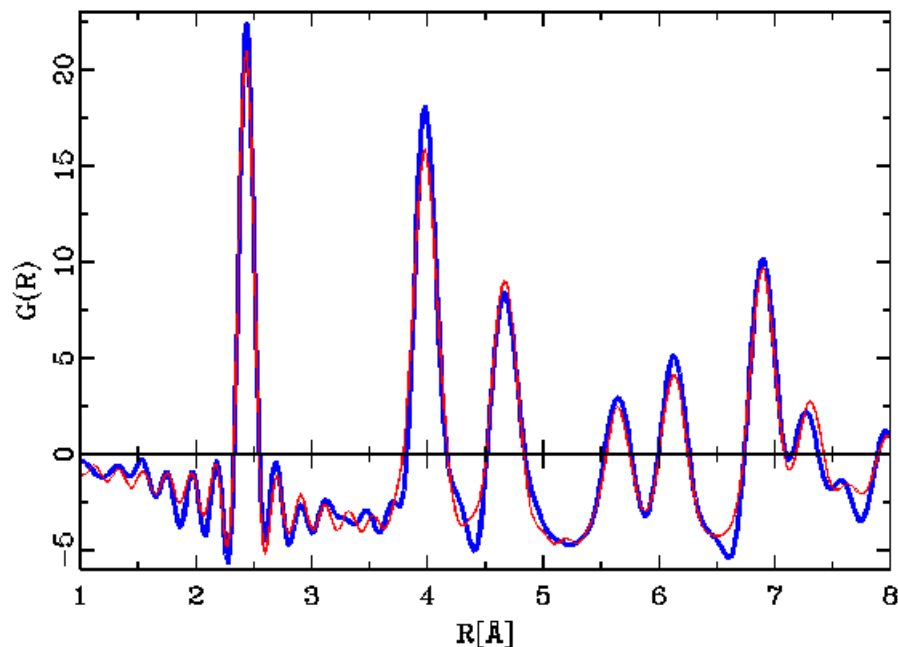
Example: ZnSe nanoparticles - Results



C. Kumpf, R.B. Neder et al., **Structure determination of CdS and ZnS nanoparticles: Direct modeling of synchrotron-radiation diffraction data**, *J. Chem. Phys.* **123**, 224707 (2005).

— exp
— calc

- Results:
 - $a=3.973\text{\AA}$, $c=6.494\text{\AA}$
 - Diameter $\sim 26\text{\AA}$
 - Stacking fault prob. 70%



Get started at

<http://skywalker.lansce.lanl.gov/lujan/instruments/NPDF/school.shtml>